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(71) Applicant: UOP Inc.  
10 UOP Plaza Algonquin & Mt. Prospect Roads  
Des Plaines Illinois 60016(US)

(72) Inventor: Lester, George Ronald  
318, Meacham Avenue  
Park Ridge Illinois(US)

(72) Inventor: Welsh, Lawrence Brian  
2203 Lincolnwood Drive  
Evanston Illinois(US)

(74) Representative: Hale, Stephen Geoffrey et al,  
J.Y. & G.W. Johnson Furnival House 14/18 High Holborn  
London WC1V 6DE(GB)

(54) Method for the preparation of integral shaped replications of shaped, porous and dissolvable materials for use as adsorbents in fixed bed adsorption processes.

(57) Integral shaped replications which may be used as supports for catalysts or as adsorbents comprise a carbonaceous pyropolymer structure which has been prepared by treating a substrate material with an organic pyrolyzable precursor compound and pyrolyzing the precursor at 500 to 1200°C. in a reducing atmosphere to form a carbonaceous pyropolymer possessing recurring units containing at least carbon and hydrogen atoms on the surface of the substrate material. This carbonaceous pyropolymer duplicates the physical shape and dimensions of the substrate material as well as a substantial portion of the pore structure thereof. The integral shaped replications possess an apparent bulk density (ABD) which is 25 to 100% of the ABD of the inorganic support, and have a crush strength of from 0.5 to 14 kilograms. The composite comprising the carbonaceous pyropolymer on the surface of the substrate material is then leached with a dissolving agent to remove the substrate material, thus leaving a shaped replication of particle aggregates. If so desired, the shaped replication may be further treated by depositing at least one inorganic oxide on each surface of the replication and/or by depositing at least one catalytically active metal and optionally removing the carbonaceous pyropolymer by oxidation.

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Method for the preparation of integral shaped  
replications of shaped, porous and dissolvable  
materials for use as adsorbents in fixed bed  
adsorption processes.

This invention relates to a method for the preparation of an integral shaped replication of a shaped, porous and dissolvable substrate material which possesses physical dimensions, shape and an apparent bulk density (hereinafter referred to as ABD) suitable for use as an adsorbent in a fixed bed adsorption process. More specifically, the invention is concerned with the preparation of materials which may be used as supports for chemically active metals, as molecular sieves, or as adsorbents which may be themselves utilized in a fixed bed adsorption process.

In many instances, it is preferred to utilize various supports upon which catalytically active metals are deposited to form catalytic compositions of matter which are useful in catalyzing various chemical reactions. Usually it is preferred to employ supports which possess a relatively high surface area whereby a greater amount of catalytically active metal may be deposited on the surface. One such support which has been employed in the past comprises a refractory inorganic oxide such as alumina, especially gamma-alumina, which possesses the aforesaid high surface area. Other forms of alumina which also have been employed will include eta- and theta-alumina, these inorganic oxides also possessing relatively high surface areas which may range from 10 to 500 m<sup>2</sup>/g. In addition to this type of catalyst support, it is also known from U.S. Patent 4,090,978 that electrocatalysts may be used in the preparation of electrodes for an electrochemical fuel cell. The support for an electrochemical catalyst employed in that patent uses a carbonaceous pyropolymer powder or particle upon which is impregnated a catalytic metal. However, as stated, the

support is in particle form which is in contradistinction to the supports of the present invention which are shaped, that is, said supports possess a definite shape, for example as a sphere, plate, fiber or monolith. The catalytic particles are blended with polytetrafluoroethylene (PTFE) powder, a binding material, and thereafter a sheet containing the catalyst is formed by a calendering or rolling operation following which the alumina is then catalytically leached from the electrode sheet. However, the formation of the sheet requires a PTFE binder and is not a replication of any starting shape, but is formed by a calendering operation. The electrocatalyst powder of this patent, after being combined with a binder, is shaped into the desired form by means of a mold press or by any other technique possessing extremely different properties than those which are possessed by the integral shaped replications of the present invention. For example, the pore structure as measured by nitrogen adsorption or desorption, or by mercury intrusion, would be very different, inasmuch as it would be changed by the presence of a binder material and by the loss of that pore structure which results from individual particles being physically bonded together. Other differences between the particles of the patent and the integral shaped replications of the present invention would be in chemical properties, electrical properties, terminal properties and mechanical properties. The chemical properties of the two composites would differ substantially, inasmuch as the presence of the binders would modify the chemical properties of the powder; the terminal properties would differ in that by using a binder with the powder, the use of a support would be limited to reactions occurring at temperatures well below 300°C. as opposed to the integral shaped replications which would be stable at temperatures in excess of 500°C. in non-oxidizing environments, or in crush strength in which the crush strength of the integral shaped replications

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is determined by the nature of the carbonaceous pyropolymer as opposed to the composite requiring a binder to hold its shape, the crush strength of such a material as being primarily determined by the crush strength of the binder material. While the patent demonstrates that micron size pyropolymer particles can be prepared from individual alumina particles which are made up of individual alumina crystalites which are strongly and chemically bonded together, the formation of relatively large spheres, plates, rods etc. which are made up of aggregates of such particles could be successfully leached after deposition of a carbonaceous pyropolymeric coating comprising recurring units containing at least carbon and hydrogen atoms to yield a macroscopic integral shaped replication of the original inorganic shaped structure.

In addition, U.S. Patent 3,964,933 describes carbon particles which may be used for electrodes and a method for the manufacture thereof. However, the composition comprises a non-conductive oxide having a deposit of carbon, and not a carbonaceous pyropolymer, on the surface. The amount of carbon deposited on the surface of the oxide may be altered by extracting or leaching a portion of the oxide to provide a material which contains from 50 to 90% by weight of carbon, the remainder of the material consisting of the oxide. As will hereinafter be shown in greater detail, this is in contradistinction to the composition of the present invention.

The use of various supports for catalytically active metals constitutes an important variation by which the reactions of various catalysts can be modified or improved. As hereinbefore set forth, in many instances the surface area of the support upon which the catalytically active metal is deposited is important, a relatively large surface area being a desirable characteristic of the support. The catalytically active composites are

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useful in a wide variety of chemical reactions and have been used in reforming reactions and hydrocracking reactions, amongst others. It is contemplated within the scope of this invention that the supports which are prepared according to the method of the invention may be used as a catalyst base such as a support for phosphoric acid to form solid phosphoric acid and thus be used in polymerization reactions, as a catalyst support for ammonia synthesis, as a support for a metal phthalocyanine complex which would form a catalyst useful for the sweetening of petroleum products such as gasoline, or as a support for an immobilized enzyme system, amongst other uses. The shaped replications which are prepared according to the method of the invention may be in any form such as those hereinbefore set forth in greater detail, said shapes possessing desirable characteristics, e.g. of surface area, pore volume, ABD and crushing strength, said integral shaped replications thereby being useful in fixed bed adsorption processes without undergoing physical deterioration to form powders, dust or fines and thus limit the use of such a composite.

According to the invention there is provided a method for the preparation of an integral shaped replication of a shaped, porous and dissolvable substrate material which possesses physical dimensions, shape and ABD suitable for use as an adsorbent in a fixed bed adsorption process, the replication duplicating the physical shape and dimensions of the substrate material and a substantial portion of the pore structure thereof, which replication consists essentially of a carbonaceous pyropolymer possessing recurring units containing at least carbon and hydrogen atoms and which replication has an ABD which is from 25 to 100% of the ABD of the substrate material, characterised in that the method comprises the steps of:

(a) treating the substrate material with an organic

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pyrolyzable precursor compound in a reducing atmosphere at a temperature in the range from 500° to 1200°C. to pyrolyze the organic compound to form the carbonaceous pyropolymer possessing recurring units containing at least carbon and hydrogen atoms in the pore structure of the substrate material,

(b) continuing the treatment of step (a) until the total accumulation of the carbonaceous pyropolymer in the pore structure of the substrate material is sufficient to result in a replication which possesses a crush strength of from 0.5 to 14 kg, and

(c) recovering the integral shaped replication comprising a carbonaceous pyropolymer possessing recurring units containing at least carbon and hydrogen atoms by leaching the substrate material from the product of step (b) by contacting said product with a dissolving agent for the substrate material under conditions selected to dissolve substantially all of the substrate material.

The steps (a) - (c) in the method of the invention may be followed by the steps of:

(d) depositing at least one refractory oxide on each surface of the integral shaped replication comprising the carbonaceous pyropolymer;

(e) removing the carbonaceous pyropolymer by oxidation; and

(f) recovering the resulting refractory oxide shaped replication.

In one preferred embodiment the substrate material is an alumina, the organic pyrolyzable precursor compound is benzene and the dissolving agent comprises phosphoric

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acid. In such an embodiment aluminium oxide may preferably be deposited on each surface of the carbonaceous pyropolymer, the carbonaceous pyropolymer removed by  
5     subjecting the composite to oxidation at a temperature in the range from 200° to 800°C. in an atmosphere of air, and the resulting refractory oxide shaped replication recovered.

The integral shaped replication supports obtained by the method of the invention comprise integral shaped  
10     replications of particle aggregates and may be prepared by treating an inorganic substrate material of the type hereinafter set forth in greater detail in any desired shape, such as spheres, plates, pellets, rods, fibers or monoliths, with the pyropolymer precursor. The amount  
15     of carbonaceous pyropolymer which is deposited on the surface of the substrate material will be sufficient to duplicate the physical shape and dimensions of the substrate material as well as a substantial portion of the pore structure thereof. In addition, the carbonaceous  
20     pyropolymer which forms the integral shaped replication will possess an ABD which is from 25 to 100% of the AET of the substrate material and the replication will possess an average crush strength which may range from 0.5 to  
25     14 kg or more, the crush strength being dependent upon the size and shape of the replication.

In preferred embodiments of the present invention, the inorganic substrate material which acts as a support has a surface area of from 1 to 500 m<sup>2</sup>/g as well as a pore structure which includes both micropores and macro-  
30     pores. For purposes of this invention, the term "micropores" denotes those pores of 300 Å or less diameter, while macropores are those greater than 300 Å in diameter. The pore strength of the shaped replications will substantially duplicate the pore structures of the substrate  
35     material, this being especially true of the pore structure as to macropores. In addition, the integral shaped repli-

cation will possess the original pore volume of the substrate material and, in addition, the pore volume which was occupied by the substrate will be now available to the integral shaped replication after removal of the substrate material. Illustrative examples of substrate materials include refractory oxides such as alumina in various forms, e.g. gamma-alumina, eta-alumina and theta-alumina, or mixtures of inorganic refractory oxides, e.g. zeolites, silica-alumina, silica-zirconia, zirconia-titania and zirconia-alumina. As hereinbefore set forth, the substrate material can have any desired shape. The particular shape of the substrate material can be obtained by any method known in the art, e.g. marumerizing, pelletizing or nodulizing, whereby a substrate material can be obtained which possesses definite pore size.

In one method of preparing the shaped replication, the substrate material, e.g. a refractory oxide, is heated to a temperature of from 400° to 1200°C. in a reducing atmosphere containing an organic pyrolyzable precursor compound for the carbonaceous pyropolymer.

The organic pyropolymer precursors preferably used for the purposes of this invention are aliphatic hydrocarbons, aliphatic halogen derivatives, aliphatic oxygen derivatives, aliphatic sulfur derivatives, aliphatic nitrogen derivatives, organometallic compounds, alicyclic compounds, aromatic compounds and heterocyclic compounds. Of the aliphatic hydrocarbons, the more common classes which may be utilized are alkanes, alkenes, alkynes, and alkadienes. Ethane, propane, butane and pentane are among the alkanes which may be successfully used. Similarly, alkenes which can be used successfully include ethene, propene, 1-butene, 2-butene and 1-pentene. Alkynes which may be successfully used include ethyne, propyne, 1-butyne, 2-butyne, 1-pentyne and 1-hexyne. 1,3-Butadiene and isoprene are among the alkadienes which may be utilized. Among the aliphatic halogen derivatives



which may be utilized are monohaloalkanes such as chloromethane, bromoethane, 1-iodopropane and 1-chlorobutane. Polyhaloalkanes such as carbon tetrachloride, chloroform, 1,2-dichloroethane and 1,2-dichlorobutane may also be  
5 utilized. An unsaturated halo compound which may be utilized is chloroprene.

The aliphatic oxygen derivatives which may be used include the classes of alcohols, ethers, halohydrides and alkene oxides, saturated aldehydes and ketones,  
10 unsaturated aldehydes and ketones, ketenes, acids, esters, salts and carbohydrates. Alcohols which may be utilized include ethanol, 2-butanol, 1-propanol, glycols (e.g. 1,3-propanediol) and glycerol. Ethers which may be utilized include ethyl ether and isopropyl ether. Appropriate  
15 halohydrins and alkene oxides include ethylene chlorohydrin, propylene chlorohydrin, ethylene oxide and propylene oxide. Suitable saturated aldehydes and ketones include formaldehyde, acetaldehyde, acetone and ethyl methyl ketone. Unsaturated aldehydes and ketones which  
20 may be used include propenal, trans-2-butenal and butenone. Ketene has also been successfully used. Likewise, formic acid, acetic acid, oxalic acid, acrylic acid, chloroethanoic acid, formic anhydride and formyl chloride may also be utilized. Esters such as methyl formate,  
25 ethyl formate and ethyl acetate may also be used. Salts such as sodium formate, potassium acetate and calcium propionate may be utilized, as may a variety of carbohydrates.

The broad classification of aliphatic sulfur derivatives which may be used may be broken down into the sub-  
30 classes of alkanethiols, alkylthioalkanes, sulfonic acids, and alkyl sulfates and alkyl metallic sulfates. Suitable among the alkanethiols are ethyl mercaptan and n-propyl mercaptan. Among the alkylthioalkanes usable are the  
35 thioethers, alkyl sulfides, methyl sulfide, ethyl sulfide

and methyl propyl sulfide. Ethyl sulfonic acid and n-propyl sulfonic acid are sulfonic acids which may also be successfully used. Ethyl sulfate and sodium lauryl sulfate are also appropriate for use.

5       The broad class of aliphatic nitrogen derivatives which may be used may be broken down into the subclasses of nitroalkanes, amides, amines, nitriles and carbyl-  
amines. Nitroethane and 1-nitropropane are examples  
of suitable nitroalkanes while acetamide and propionamide  
10 are among the appropriate amides. Amines such as dimethylamine and ethylmethanamine, nitriles such as acetonitrile and propionitrile, and carbylamines such as ethyl isocyanide may also be used. Organometallic  
compounds such as tetraisopropyl titanate, tetrabutyl  
15 titanate and 2-ethylhexyl titanate may also be used.

Particularly preferred for use as the organic pyro-  
lyzable precursor compound in the method of this invention  
are alicyclic compounds. Foremost among these are cyclo-  
hexane and cyclohexene. Aromatic compounds, including  
20 the subclasses of hydrocarbons, halogen compounds, oxygen derivatives, ethers, aldehydes, ketones, quinones, aromatic acids, aromatic sulfur derivatives and aromatic nitrogen compounds, may also be utilized. Among the  
many suitable aromatic hydrocarbons, benzene, naphthalene,  
25 anthracene, and toluene have been successfully utilized. Benzyl chloride and benzal chloride are appropriate halo-  
gen compounds while phenol, o-cresol, benzyl alcohol and hydroquinone are among the suitable derivatives.

Ethers, such as anisole and phenetole, and aldehydes,  
30 ketones and quinones, such as benzaldehyde, acetophenone, benzophenone, benzoquinone and anthraquinone, may also be used. Aromatic acids such as benzoic acid, phenyl-  
acetic acid, and hydrocinnamic acid may be utilized while  
the aromatic sulfur derivative benzene sulfonic acid  
35 will also serve successfully. The aromatic nitrogen

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compounds nitrobenzene, 1-nitronaphthalene, aminobenzene and 2-amino toluene may also be successfully used. Among heterocyclic compounds which may be used, 5-membered ring compounds such as furan, proline, coumarone, thio-  
5 naphthene, indole, indigo and carbazole may be mentioned. 6-Membered ring compounds such as pyran, coumarin and acridine may also be utilized.

As can be seen, an extremely wide latitude can be exercised in the selection of the organic pyrolyzable  
10 precursor compound, since virtually any organic material that can be vaporized, decomposed and polymerized on the refractory oxide by heating will suffice. The resultant carbonaceous pyropolymer will possess recurring units containing at least carbon and hydrogen atoms;  
15 however, depending upon the pyropolymer precursor which has been selected, the pyropolymer may also contain other atoms such as nitrogen, oxygen, sulfur, phosphorus or metals.

In another method of preparing the shaped replication  
20 the substrate material, e.g. a refractory inorganic oxide, is impregnated with a solution of a carbohydrate material, e.g. dextrose, sucrose, fructose or starch, and thereafter the impregnated support is dried and then subjected to a pyrolysis temperature in the range from 400 to 1200°C,  
25 whereby a carbonaceous pyropolymer possessing recurring units containing at least carbon and hydrogen atoms and having an ABD of from 25 to 100% of the ABD of the substrate material is formed in at least a monolayer on the surface of the substrate material.

30 Whichever method is used, the resulting composite will possess the carbonaceous pyropolymer on the surface of the substrate material in a sufficient quantity so that the carbonaceous pyropolymer possesses an average crush strength of from 0.5 to 14 kg as well as an ABD

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of from 25 to 100% of the ABD of the substrate material. Preferably, the carbonaceous pyropolymer contains from 15 to 50% by weight of carbon. In addition, the pore structure of the carbonaceous pyropolymer will duplicate  
5 a substantial portion of the pore structure, both macro-pore and micropore in nature, of the substrate material.

Following this, the substrate material is chemically leached from the carbonaceous pyropolymer. The leaching is effected by treating the composite with a dissolving  
10 material which in the case of an inorganic oxide substrate material is conveniently either an acid or a base and results in the formation of a high surface area carbonaceous pyropolymer support which is a shaped replication of the original shaped substrate material. The leaching  
15 of inorganic oxide substrate materials may be effected over a wide range of temperatures, e.g. from ambient temperature (20°-25°C,) up to 250°C. or more, for a period of time which may range from less than 1 hour up to 72 hours or more. It is to be understood that the operating  
20 parameters of the leaching step will vary over a wide range and will be dependent upon a combination of factors such as time, temperature and strength of the leaching solution. Examples of acids and bases which may be utilized to leach out the inorganic oxide substrate mater-  
25 ial are inorganic acids, e.g. phosphoric acid, sulfuric acid, nitric acid and hydrochloric acid, organic acids, e.g. methyl sulfonic acid, ethyl sulfonic acid, propyl sulfonic acid and toluene sulfonic acid, and strong bases, e.g. sodium hydroxide, potassium hydroxide, lithium hydr-  
30 oxide, rubidium hydroxide and cesium hydroxide. It is to be understood that the aforementioned dissolving materials are only representative of the class of compounds which may be used and that any chemical which is capable of removing the refractory inorganic oxide while retaining  
30 the high surface area of the carbonaceous pyropolymer may be used

As hereinbefore set forth the resulting shaped replications will possess a high surface area and a desirable pore volume and ABD, as well as possessing a high crush strength. They may therefore be utilized as a support  
5 for catalysts, immobilized enzymes, or even as molecular sieves and adsorbents.

The carbonaceous pyropolymer replication may be used as such or, if so desired, it may be used as a support upon which at least one inorganic oxide may be  
10 deposited. The carbonaceous pyropolymer replications may be impregnated with solutions containing the desired refractory oxide or a combination of refractory oxides. The impregnation of the carbonaceous pyropolymer structures may be effected by treating said structures with  
15 either a solution containing a soluble salt of the desired metal or a sol thereof. For example, the carbonaceous pyropolymer replications may be impregnated with an alumina sol, a zirconium oxide sol, a titanium oxide sol or mixtures thereof in order to produce a composition  
20 comprising a shaped replication of particle aggregates comprising the carbonaceous pyropolymer atoms having at least one refractory oxide deposited on all surfaces thereof. The refractory oxides which may be utilized comprise the oxides of aluminium, boron, cerium, barium,  
25 copper, nickel, chromium, molybdenum, zirconium, titanium, hafnium, vanadium, tungsten, magnesium, silicon, tin and lead. As an alternative method of impregnating the carbonaceous pyropolymer replications, it is possible to utilize an aqueous solution of a salt of the desired  
30 metal which may then be converted to the corresponding oxide by conventional means such as oxidation. Some representative examples of salts of the metals which may be used are organic salts such as aluminium acetate, aluminium propionate, aluminium succinate, aluminium  
35 sulfate, zirconium acetate, zirconium propionate, zirconium succinate, zirconium sulfate, titanium acetate, titan-

ium propionate, titanium succinate, titanium sulfate, silicon acetate, silicon propionate, silicon succinate and silicon sulfate. In addition, metal-organic complexes such as aluminium acetylacetonate, silicon acetylacetonate, 5 zirconium acetylacetonate, titanium acetylacetonate cerium acetylacetonate, barium acetylacetonate copper acetylacetonate, nickel acetylacetonate, chromium acetylacetonate, molybdenum acetylacetonate or complexes which are formed between the aforementioned metals and ethylene 10 diamine tetraacetic acid may also be used to impregnate the carbonaceous pyropolymer replications, said soluble salts and complexes being subsequently converted to the desired metallic oxide by conventional means such as heat treatment or oxidation at an elevated temperature. 15 It is to be understood that the aforementioned metals and salts thereof are only representative of the type of compounds which may be used to impregnate the carbonaceous pyropolymer structure. The resulting composition will possess a modified pore structure, its final pore 20 structure being determined by the combination of the pore structure of the starting substrate material, the properties of the carbonaceous pyropolymer replication, the thickness of the impregnated refractory oxide layer(s), and the fact that all surfaces of the carbonaceous pyropolymer are coated with the refractory oxide. 25 In many instances, the surface area of the original starting support normally will be increased, inasmuch as both sides of the carbonaceous pyropolymer replications are now coated with the refractory oxide.

30 If so desired, the compositions comprising the shaped replications having at least one refractory oxide deposited on all surfaces thereof may be utilized as catalysts by having a catalytically active metal either impregnated on the refractory oxide or sealed into the refractory 35 oxide. The addition of the catalytically active metal may be effected by utilizing either a co-impregnation,

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a prior impregnation, or a subsequent impregnation of the carbonaceous pyropolymer replication. Examples of catalytically active metals which may be used include platinum, palladium, rhodium, ruthenium, germanium, tin and nickel, either alone or in combinations of two or more thereof. For example, the impregnation may be effected by treating the carbonaceous pyropolymer replication with an aqueous or organic solution of the desired metal or combination of metals in an amount sufficient to deposit at least one catalytically active metal on the surface of the carbonaceous pyropolymer replication in an amount ranging from 0.1 to 20% by weight. For example, a mixture of platinum and rhenium, platinum and ruthenium, platinum and tungsten, platinum and nickel, platinum and rhodium, platinum and lead, platinum and germanium, palladium and rhenium, palladium and rhodium, palladium and tungsten, palladium and nickel, palladium and ruthenium, palladium and lead, or palladium and germanium may be impregnated on the carbonaceous pyropolymer replication. The solution which is utilized to impregnate the carbonaceous pyropolymer replication is preferably aqueous in nature, some specific examples of these aqueous solutions being solutions of chloroplatinic acid, chloroplatinous acid, bromoplatinic acid, sodium platinate, potassium platinate, lithium platinate, platinic chloride and platinous chloride, as well as solutions of corresponding compounds of palladium, ruthenium, tin, tungsten, germanium and rhodium, and mixtures thereof. After impregnation of the structure, which may be carried out for from 0.5 hour to 10 hours or more, the solvent may be removed by heating to a temperature in the range of from 100 to 400°C., the temperature being that which is sufficient to evaporate said solvent and leave the metal or mixtures of metals impregnated on the surface of the carbonaceous pyropolymer replication. Thereafter the structure may then be dried at elevated temperatures e.g. ranging from 100 to 200°C., for a period

of time e.g. ranging from 2 to 6 hours or more. Thereafter, the metal impregnated carbonaceous pyropolymer structure is subjected to a reducing step in the presence of a reducing atmosphere or medium such as hydrogen at  
5 elevated temperature, e.g. from 200 to 600°C. or more, preferably 250 to 400°C., for a period of time, e.g. ranging from 0.5 or 1 hour up to 4 hours or more, whereby the metallic compound is reduced to the metal in the form of particles. By utilizing a metallic impregnation  
10 prior to impregnating the carbonaceous pyropolymer support with a solution or sol corresponding to the refractory oxide, the catalytically active metal will be sealed into the refractory oxide layer when the latter is formed. Conversely speaking, the metal impregnation step herein  
15 described may be effected using a co-impregnation technique or subsequently impregnating the composition in which the carbonaceous pyropolymer replication contains at least one refractory inorganic oxide on all surfaces thereof, thereby having the catalytically active metals  
20 impregnated on the surface of the refractory oxide.

If so desired, following the deposition of at least one refractory oxide on all surfaces of the carbonaceous pyropolymer replication, either with or without the presence of a catalytically active metal, the aforesaid  
25 carbonaceous pyropolymer may be removed, thus leaving a refractory oxide or mixture of refractory oxides which is a shaped replication of the carbonaceous pyropolymer replication but which possesses a surface area which may be up to several times the surface area of the  
30 original substrate material. The removal of the carbonaceous pyropolymer may be accomplished by treating the shaped replication composition of matter at an elevated temperature in the presence of an oxidizing agent such as an oxygen-containing gas. This treatment may be  
35 effected at a temperature ranging from 200 to 800°C. with the concentration of the oxygen in the atmosphere ranging from 0.1 to 21% by volume. The removal of the



carbonaceous pyropolymer may also be effected over a period of time ranging from less than 1 hour to 10 hours or more in duration, the operating parameters of temperature, time, and oxygen content being dependent upon the thickness and extent of graphitization of the carbonaceous pyropolymer as well as the physical and chemical properties thereof. For example, one method of effecting the removal of the carbonaceous pyropolymer is to treat the composition at a temperature of 200°C. for a predetermined period of time and thereafter to increase the temperature at a predetermined rate until the upper portion of the operating range has been reached and maintain the temperature at this point for a period of time sufficient to remove all of the aforesaid carbonaceous pyropolymer. Thereafter the refractory oxide shaped replication may be used, e.g. as a catalyst support, molecular sieve or adsorbent, or if it contains a catalytically active metal such as those hereinbefore set forth, as a catalyst per se.

The shaped replications may be prepared in any suitable manner including both batch and continuous types of operations. For example, when a batch type of operation is employed an inorganic substrate material such as an alumina of the type hereinbefore set forth in greater detail may be dried and placed in a reducing atmosphere. Following this, the organic pyrolyzable precursor compound also in a reducing atmosphere may be passed over the inorganic substrate material at an elevated temperature of from 400 to 1200°C. for a period of time sufficient to pyrolyze the precursor compound while impregnating the substrate material. Alternatively, the inorganic substrate material such as a refractory oxide may be impregnated with an aqueous solution of a carbohydrate such as sucrose or dextrose, the impregnated substrate material dried at an elevated temperature, and thereafter the dried impregnated substrate material

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pyrolyzed at a temperature in the range hereinbefore set forth for a predetermined period of time sufficient to form at least a monolayer of the carbonaceous pyropolymer on the substrate material. It is to be understood  
5 within the scope of this invention that the thickness of the carbonaceous pyropolymer on the substrate material may vary from one monolayer to several monolayers depending on the amount of precursor compound used as well as on the operating parameters of time and temperature.

10 After recovering the resulting composite, it is then subjected to a leaching step in an appropriate apparatus, for example by immersion in an acid such as a 96% phosphoric acid solution at an elevated temperature, e.g. from 50° up to 150°C. or more, for a predetermined  
15 period of time. Following the leach step the shaped replication of particle aggregates comprising the carbonaceous pyropolymer is recovered, washed and dried and optionally treated for deposition of a refractory oxide and/or a catalytically active metal and optional removal  
20 of the carbonaceous pyropolymer itself, as hereinbefore set forth.

In addition to the batch type of operation hereinbefore discussed, the shaped replication may also be prepared in a continuous manner of operation. For  
25 example, when such a type of operation is to be employed an inorganic substrate material, preferably possessing a high surface area, is continuously passed through a pyrolysis zone wherein it is contacted with an organic pyrolyzable precursor compound at an elevated temperature  
30 in the range of from 400° to 1200°C. whereby a carbonaceous pyropolymer containing recurring carbon and hydrogen atoms is deposited on the surface of said substrate material. By varying the operating parameters of time, temperature and particular pyropolymer precursor, the  
35 thickness of the carbonaceous pyropolymer on the surface

of the inorganic substrate material can be adjusted to a predetermined size. After the predetermined depth of the carbonaceous pyropolymer on the surface of the substrate material has been attained, it is recovered  
5 from the pyrolysis zone and continuously charged to a leaching bath. In the leaching bath the substrate material is leached from the composite, utilizing for example in the case of an inorganic oxide substrate material an acid such as phosphoric acid or a strong base such  
10 as sodium hydroxide in an appropriate strength at elevated temperatures within the range hereinbefore set forth. Upon completion of the leach the carbonaceous pyropolymer replication is continuously withdrawn from said bath and, in one embodiment of the invention, continuously charged  
15 to either a sol or a solution of a metal salt wherein it is coated with a salt corresponding to at least one refractory metal oxide, all surfaces of the carbonaceous pyropolymer replication being coated. Again, as in the case of the pyrolysis step, the thickness of the layer  
20 of one refractory oxide or a mixture of refractory oxides may be varied by predetermining the operating parameters of time and solution strength of the soluble salt of the transition metal. After passage through the bath or sol, the composition comprising a shaped replication  
25 of particle aggregates comprising a carbonaceous pyropolymer having at least one refractory oxide or precursor deposited on all surfaces thereof is continuously withdrawn and passed to a drying oven wherein the solvent such as water is removed. Thereafter, if desired, the  
30 composition may be recovered and used, e.g. as a catalyst base, adsorbent or molecular sieve, or it may be continuously passed to an oxidation zone wherein it is subjected to an oxidation step in the presence of an oxidizing agent such as water or an oxygen-containing gas such  
35 as air or oxygen at an elevated temperature in the range of from 200 to 800°C., whereby the carbonaceous pyropolymer structure is removed, thus leaving a shaped replication of the refractory metal oxide or mixture of refrac-

tory metal oxides possessing essentially the same shape as the original inorganic support but also possessing a surface area several times that of the original support.

5 In another embodiment of the invention, after formation of the carbonaceous pyropolymer replication by leaching out the inorganic substrate material the replication may then be impregnated with a catalytically active metal by continuous passage through an aqueous solution of such metal prior to passage through the solution or  
10 sol wherein at least one refractory oxide is deposited on the surface. Another variation consists in passing the refractory oxide coated carbonaceous pyropolymer replication through an impregnating solution of the catalytically active metal and thereafter drying the  
15 impregnated composition. In both instances the impregnated composition is continuously passed through a reducing zone wherein it is contacted with hydrogen at an elevated temperature to reduce the catalytically active metal to the elemental form.

20 The following Examples illustrate the invention without limiting it.

#### EXAMPLE I

A shaped replication support was prepared by calcining 3.2 mm diameter alumina spheres having a surface  
25 area of  $147 \text{ m}^2/\text{g}$ , a pore volume of  $0.42 \text{ ml/g}$  and an ABD of  $0.377 \text{ g/ml}$  at a temperature of  $482^\circ\text{C}$ . for a period of 2 hours. Following this the spheres were placed in an inert atmosphere and a carbonaceous pyropolymer layer was deposited on these spheres by pyrolyzing cyclo-  
30 hexane in the presence of said spheres at a temperature of  $788^\circ\text{C}$ . in an inert atmosphere.

The resulting composite material was then leached by immersion in a 96% phosphoric acid solution at a

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temperature of 160°C. for a period of 24 hours. The resulting shaped replication of particle aggregates comprising a carbonaceous pyropolymer structure possessing recurring units of carbon and hydrogen atoms was analyzed and it was found that the alumina content was only 0.27 wt.%, thus indicating that essentially all of the alumina had been removed in the leach. The carbonaceous pyropolymer structure in the form of spheres was found to have a BET surface area of 656 m<sup>2</sup>/g, an ABD of 0.17 g/ml and a crushing strength of 7 kg. To further illustrate the differences between the initial inorganic support and the shaped replication in the form of a carbonaceous pyropolymer structure, the shape of which was a replication of the shape of the initial refractory inorganic oxide support, various characteristics are set forth in the following table.

	<u>Feed</u>	<u>Product</u>
Composition	Alumina	Carbonaceous Pyropolymer
Bulk Density	0.38 g/ml	0.17 g/ml
Size	3.2 mm Spheres	3.2 mm Spheres
Pore Volume, <600 Å	1.10 ml/g	1.84 ml/g
Pore Volume, >600 Å	0.17 ml/g	1.26 ml/g
Pore Volume/Bed Volume		
<600 Å	0.42 ml/ml	0.31 ml/ml
>600 Å	0.07 ml/ml	0.21 ml/ml
Total	0.49	0.52
Surface Area, m <sup>2</sup> /g	147 m <sup>2</sup> /g	656 m <sup>2</sup> /g
Surface Area/Bed Volume	55.9 m <sup>2</sup> /ml	111.5 m <sup>2</sup> /ml
Volume or Solid/Bed Volume	0.12 ml/ml	0.074 ml/ml

It is therefore readily apparent from the above table that the shaped replication of particle aggregates which comprised a carbonaceous pyropolymer containing at least recurring carbon and hydrogen atoms possessed a bulk density approximately ½ of the bulk density of the original support, was of the same size, had an increased pore volume and a surface area which was approximately

4.5 times greater than that of the original support. The increased surface area thus renders the support of greater value for the deposition of catalytically active metals for further use as a catalyst in various hydrocarbon reactions.

#### EXAMPLE II

The shaped replication of particle aggregates comprising a carbonaceous pyropolymer possessing recurring units of carbon and hydrogen atoms which was prepared according to the above example was then impregnated with a refractory oxide. The impregnation was effected by heating the shaped replication under vacuum at a temperature of about 100°C. to drive off adsorbed water. After allowing the particle aggregates to cool, the particle aggregates which were in the form of spheres were subjected to multiple impregnations with a 100% solution of titanium-2-propoxide under vacuum. After allowing the impregnation to occur for a period of about 2 hours, the excess solution was drained and the spheres were washed with 2-propanol under a nitrogen atmosphere. After washing with the 2-propanol, the spheres were then washed in air and subjected to hydrolysis to form a composition of matter comprising a shaped replication of particle aggregates comprising a carbonaceous pyropolymer possessing recurring units of carbon and hydrogen atoms having a titanium dioxide coating deposited on the surface thereof.

#### EXAMPLE III

The titanium dioxide coated spheres which were prepared according to the above paragraph were then subjected to an oxidation procedure in which the spheres were heated in an oxygen containing atmosphere at a temperature of from 540° to 750°C. for a period of about 8 hours. At the end of this period the spheres were recovered and analyzed for crystal structure. The titanium dioxide

spheres were found to comprise a mixture of anatase and rutile, no titanium, titanium carbide, or carbon being found by this analysis. It is therefore apparent that by utilizing the process of this invention it is possible to obtain a shaped replication of an initial support, said shaped replication comprising either particle aggregates consisting of carbonaceous pyropolymer possessing recurring units of carbon and hydrogen atoms depending upon the pyropolymer precursor which is employed; a refractory oxide coated shaped replication of particle aggregates, the thickness of the refractory oxide being dependent upon the particular refractory oxide which is employed as well as the number of impregnations; or a shaped replication of a refractory oxide alone, the carbonaceous pyropolymer having been removed by conventional oxidation treatments.

CLAIMS

1. A method for the preparation of an integral shaped replication of a shaped, porous and dissolvable substrate material which possesses physical dimensions, shape and an apparent bulk density (ABD) suitable for use as an adsorbent in a fixed bed adsorption process, the replication duplicating the physical shape and dimension of the substrate material and a substantial portion of the pore structure thereof, which replication consists essentially of a carbonaceous pyropolymer possessing recurring units containing at least carbon and hydrogen atoms and which replication has an ABD which is from 25 to 100% of the ABD of the substrate material, characterised in that the method comprises the steps of:

(a) treating the substrate material with an organic pyrolyzable precursor compound in a reducing atmosphere at a temperature in the range from 400° to 1200°C. to pyrolyze the organic compound to form the carbonaceous pyropolymer possessing recurring units containing at least carbon and hydrogen atoms in the pore structure of the substrate material,

(b) continuing the treatment of step (a) until the total accumulation of the carbonaceous pyropolymer in the pore structure of the substrate material is sufficient to result in a replication which possesses a crush strength of from 0.5 to 14 kg, and

(c) recovering the integral shaped replication comprising a carbonaceous pyropolymer possessing recurring units containing at least carbon and hydrogen atoms by leaching the substrate material from the product of step (b) by contacting said product with a dissolving agent for the substrate material under conditions selected to dissolve substantially all of the substrate material.

2. A method as claimed in claim 1, characterised



in that the substrate material is a high-surface area inorganic oxide selected from alumina, silica and mixtures thereof.

3. A method as claimed in claim 1 or 2, characterised in that the organic pyrolyzable precursor compound is selected from benzene, cyclohexane, dextrose and mixtures thereof.

4. A method as claimed in any of claims 1 to 3, characterised in that step (c) is followed by the step of

(d) depositing at least one refractory oxide on each surface of the integral shaped replication.

5. A method as claimed in claim 4, characterised in that step (d) is followed by the step of

(e) removing the carbonaceous pyropolymer by oxidation, thereby forming a refractory oxide shaped replication which is recovered.

6. A method as claimed in claim 4 or 5, characterised in that the refractory oxide is selected from alumina, silica, titanium oxide, zirconium oxide and mixtures thereof.

7. A method as claimed in any of claims 4 to 6, characterised in that at least one catalytically active metal is deposited on the surface of the carbonaceous pyropolymer or the refractory oxide.

8. A method as claimed in claim 7, characterised in that the catalytically active metal is selected from platinum, palladium, rhodium and mixtures thereof.

9. The use of a replication as claimed in any of claims 1 to 8 as catalyst support, molecular sieve or adsorbent.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0089425  
Application number

EP 82 30 1430

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	--- US-A-3 676 173 (ADAMS) * Column 2, lines 22-66; column 3, lines 26-60; columns 11,12; claims *	1,2	B 01 J 20/28 B 01 J 21/18 B 01 J 37/00
Y	--- DE-A-2 426 814 (U.S. ATOMIC ENERGY) * Page 7; page 8, claims 1-4 * & US - A - 4 070 514	1	
A	--- EP-A-0 002 251 (HOECHST) * Page 3, lines 1-30; page 4, lines 19-20 *	1-3,7	
A	--- US-A-4 025 689 (KAZUO KOBAYASHI) * Columns 6-8; claims *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
A	--- US-A-3 891 574 (KAZUO KOBAYASHI) * Columns 5,6; claims *	1	B 01 J C 01 B C 04 B
Y	--- FR-A-2 172 755 (NORTON CO.) * Pages 6,7; claims *	1,4,5	
A	--- US-A-4 077 908 (STENZEL) * Columns 4-6; claims *		
--- -/-			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-11-1982	Examiner WENDLING J.P.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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DOCUMENTS CONSIDERED TO BE RELEVANT			Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A	US-A-3 446 593 (MOUTAUD) * Column 2, claims *		
Y	US-A-4 039 480 (WATSON) * Column 2, line 26 - column 4, line 45 *	4-8	
D,A	US-A-4 090 978 (WELSH) * Columns 13,14; claims *	1	
D,A	US-A-3 964 933 (FUNG)		
A	US-A-3 090 094 (SCHWARTZWALDER) * Columns 5,6; claims *	4,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-11-1982	Examiner WENDLING J.P.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, r after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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